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Third-order optical response of molecular aggregates. Disorder and the breakdown of size-enhancement

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The third-harmonic generation and nonlinear absorption of linear molecular aggregates with energetic disorder are numerically simulated. A comparison is made between the local-field approximation (LFA) and exact response theory, and it is shown that the validity of the LFA does not improve in the presence of energetic disorder ranging up to the intermolecular interaction. The breakdown of size-enhancement of optical nonlinearities caused by energetic disorder is investigated and scaling laws relating the nonlinear response to the delocalization range of the exciton states are obtained.

1. Introduction

Recently, there has been a growing interest in the optical properties of molecular aggregates. One of the reasons is that, like other nanostructures, these systems may exhibit large, size-enhanced, optical nonlinearities [1,2]. Size-enhancement refers to the fact that for an aggregate small compared to an optical wavelength, the hyperpolarizabilities do not scale proportionally to the number of molecules (N) it contains, but rather like N^α , with $\alpha \geq 2$ [3–5]. Like exciton-superradiance [6], size-enhancement is a collectivity phenomenon that directly results from the intermolecular interactions, which delocalize the electronic excitations over the aggregate (Frenkel excitons) and concentrate all available oscillator strength in one or a few exciton states. It is well-known, however, that inhomogeneities (energetic disorder) tend to counteract the interactions and localize the exciton states on part of the aggregate [7,8]. If the localization range is appreciably less than the aggregate size, the enhancement must break down. Both for fundamental reasons and because of its practical implications, it is important to characterize this breakdown. In this Letter, we address this problem by numerically simulating exact expressions for the third-harmonic generation (THG) and nonlinear absorption of linear chains of coupled two-level absorbers described by the Frenkel exciton Hamil-

tonian with energetic disorder. This model is relevant for J-aggregates [8] and conjugated polymers with a small amount of charge transfer, like polysilanes [9–11]. Furthermore, we address the important question how well the local-field approximation (LFA) describes the optical response. It has recently been shown that this popular mean-field theory, which neglects quantum correlations between the molecules within an aggregate [12], does not at all recover the nonlinear absorption spectrum of *homogeneous* aggregates [13]. Based on the intuition that disorder tends to lessen the importance of interactions, one might expect that the validity of the LFA improves with growing disorder. We investigate this by also evaluating the THG and nonlinear absorption spectra within the LFA and comparing them to the exact results.

2. Model and general theory

As model system we consider a linear array of N nonpolar two-level molecules with parallel transition dipoles of magnitude μ . The chain is assumed to be small compared to an optical wavelength and is described by the standard Frenkel-exciton Hamiltonian [14],

$$\hat{H}_0 = \sum_{n,m=1}^N \hbar H_{nm} \hat{B}_n^\dagger \hat{B}_m, \quad (1)$$

where \hat{B}_n^\dagger (\hat{B}_n) denotes the Pauli creation (annihilation) operator for an excitation on molecule n . The diagonal elements of the $N \times N$ matrix H_{nm} are the molecular transition frequencies Ω_n . We allow for energetic disorder by assuming that $\Omega_n = \Omega + D_n$, with Ω the average frequency and D_n a random offset that is chosen independently for each molecule from a Gaussian with standard deviation D . The off-diagonal elements of H_{nm} are the intermolecular interactions; we restrict to nearest-neighbor interactions V , with $V < 0$ (J-aggregate). Using the Jordan-Wigner transformation from the interacting Paulions to non-interacting Fermions, all 2^N eigenstates of \hat{H}_0 can be obtained by only diagonalizing the tri-diagonal matrix H_{nm} , irrespective of the disorder [15]. This enables one to evaluate in a relatively easy way the chain's hyperpolarizabilities through standard response theory [16]. In particular, the third-order hyperpolarizability, which is the chain's lowest order nonlinearity, is then obtained as [17,18]

$$\begin{aligned} \gamma^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) \\ = \sum_{\text{perm}} \{ \gamma_r^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) \\ + [\gamma_r^{(3)}(\omega_s; -\omega_1, -\omega_2, -\omega_3)]^* \}, \end{aligned} \quad (2a)$$

with

$$\begin{aligned} \gamma_r^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) \\ = -\frac{2}{8\hbar^3} \sum_{\sigma_1, \sigma_2=1}^N \frac{1}{\omega_3 + \Omega_{\sigma_2} + i\Gamma} \\ \times \left[\frac{|\mu_{0,\sigma_1}\mu_{0,\sigma_2}|^2}{\omega_s - \Omega_{\sigma_1} + i\Gamma} \left(\frac{1}{\omega_1 - \Omega_{\sigma_1} + i\Gamma} + \frac{1}{\omega_1 - \Omega_{\sigma_2} + i\Gamma} \right) \right. \\ \left. - \sum_{\substack{\sigma_3, \sigma_4=1 \\ \sigma_3 > \sigma_4}}^N \frac{\mu_{0,\sigma_2}\mu_{\sigma_2,\sigma_3}\mu_{\sigma_3,\sigma_4}\mu_{\sigma_4,\sigma_1}\mu_{\sigma_1,0}}{(\omega_1 - \Omega_{\sigma_1} + i\Gamma)(\omega_s - \Omega_{\sigma_2} + i\Gamma)} \right. \\ \left. \times \frac{\omega_1 + \omega_2 - 2\Omega_{\sigma_2}}{\omega_1 + \omega_2 - \Omega_{\sigma_3} - \Omega_{\sigma_4} + 2i\Gamma} \right]. \end{aligned} \quad (2b)$$

In eq. (2a), the summation extends over all different permutations of the frequencies ω_1 , ω_2 , and ω_3 of the incident laser fields, and $\omega_s \equiv \omega_1 + \omega_2 + \omega_3$. The asterisk denotes complex conjugation. In eq. (2b), Ω_σ ($\sigma = 1, \dots, N$) are the eigenfrequencies of the ma-

trix H_{nm} and 2Γ is the damping rate of a molecular excited state population; pure dephasing is not included. The quantity $\mu_{0,\sigma}$ is the transition dipole between the ground state of the aggregate (with all molecules in the ground state) and the one-exciton state $|\sigma\rangle$, in which the molecules share one excitation (the conventional Frenkel excitons). The site-amplitudes of $|\sigma\rangle$ are the components $\varphi_{\sigma n}$ of the σ th normalized eigenvector of H_{nm} and its frequency is Ω_σ . We thus have: $\mu_{0,\sigma} = \mu \sum_n \varphi_{\sigma n}$. Similarly, $\mu_{\sigma,\sigma_1\sigma_2}$ denotes the transition dipole between the one-exciton $|\sigma\rangle$ and the two-exciton state $|\sigma_1\sigma_2\rangle$ ($\sigma_1 > \sigma_2$), in which the molecules share two excitations. The state $|\sigma_1\sigma_2\rangle$ has frequency $\Omega_{\sigma_1} + \Omega_{\sigma_2}$ and $\mu_{\sigma,\sigma_1\sigma_2}$ can also be expressed in terms of the eigenvectors $\varphi_{\sigma n}$ [15,18]. Above, we have for simplicity ignored the tensor nature of $\gamma^{(3)}$, so that eq. (2) is strictly valid if all incident laser fields are polarized parallel to the molecular transition dipoles; extension to the general situation is straightforward [17]. Eq. (2) is the exact expression for the third-order polarizability of a single aggregate. In order to find the macroscopic susceptibility for a sample that contains a dilute distribution of noninteracting aggregates, one has to average this expression over the energetic disorder and multiply by the average density of aggregates.

We now turn to the hyperpolarizability within the local-field approximation (LFA). In that theory, one calculates the nonlinear optical response of an assembly of interacting molecules by evaluating the response of a single molecule to a local electric field, which consists of the external fields plus a contribution describing the interactions with other molecules [16]. This scheme is based on a factorization approximation for expectation values of operators acting on different molecules and is, thus, a mean-field approximation [12]. Within the LFA the hyperpolarizability has the familiar form

$$\begin{aligned} \gamma_{\text{LFA}}^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) = \sum_n L_n(\omega_s) L_n(\omega_1) \\ \times L_n(\omega_2) L_n(\omega_3) \gamma_n^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3), \end{aligned} \quad (3)$$

where $\gamma_n^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3)$ is the third-order hyperpolarizability of molecule n , which can be written as eq. (2a), but now with

$$\gamma_{n,r}^{(3)}(-\omega_s; \omega_1, \omega_2, \omega_3) = -\frac{4\mu^4}{8\hbar^3} \times \frac{1}{(\omega_s - \Omega_n + i\Gamma)(\omega_1 - \Omega_n + i\Gamma)(\omega_3 + \Omega_n + i\Gamma)} \quad (4)$$

The local-field factors $L_n(\omega)$ reduce to unity off-resonance ($|\omega - \Omega| \gg |V|$), whereas close to resonance they are given by [18]

$$L_n(\omega) = \sum_{\sigma,m} \varphi_{\sigma n}^* \varphi_{\sigma m} \frac{\omega - \Omega_n + i\Gamma}{\omega - \Omega_\sigma + i\Gamma} \quad (5)$$

($\omega > 0$; $L_n(-\omega) \equiv L_n(\omega)^*$). It should be noted that, in contrast to eq. (2), eqs. (3)–(5) are not restricted to the linear chain configuration considered here.

It is clear that the LFA differs from the exact theory in its resonance structure: eqs. (3)–(5) do not yield the two-photon resonances that are found in eq. (2b) at $\omega_1 + \omega_2 = \Omega_{\sigma_3} + \Omega_{\sigma_4}$. If all lasers are tuned off-resonance, the two results can be shown to be equal by using sum rules for the exciton transition dipoles. Furthermore, closer inspection reveals that in the vicinity of an exciton resonance, Ω_σ , the local-field factors do not exhibit a scaling with N . This is easiest to see for homogeneous aggregates, where the $\varphi_{\sigma n}$ scale like $1/\sqrt{N}$, but also holds in the presence of disorder. In combination with eq. (3), this implies that on resonance $\gamma_{LFA}^{(3)}$ is proportional to N . Thus, *no size-enhancement is found within the LFA*. By contrast, the exact theory may exhibit an on-resonant scaling with N^2 [4,17], because in the absence of disorder, each dipole scales like \sqrt{N} provided that the aggregate is small compared to an optical wavelength.

In section 3, we present results for the third-harmonic generation and the nonlinear absorption for ensembles of disordered aggregates using the above expressions for the hyperpolarizabilities in a standard numerical simulation. The number of aggregate realizations generated at random to obtain the disorder average was typically of the order of 50000. (Much larger ensembles were used, however, to simulate the nonlinear absorption within the LFA at high disorder [18].)

3. Results and discussion

3.1. Third-harmonic generation

The intensity of THG from an ensemble of aggregates is given by $I_{THG} \propto |\langle \gamma^{(3)}(-3\omega; \omega, \omega, \omega) \rangle_d|^2$, where ω is the laser frequency and $\langle \rangle_d$ denotes the disorder average. Here, we will restrict to the situation where 3ω is resonant with the one-exciton band ($\omega \approx \frac{1}{3}\Omega$). If we only keep terms in eq. (2) that have at least one resonant factor, replace the frequencies Ω_σ in all off-resonant denominators by Ω , and use the sum rules $\sum_\sigma |\mu_{0,\sigma}|^2 = N\mu^2$ and $\sum_{\sigma_1, \sigma_3 > \sigma_4} \mu_{\sigma_2, \sigma_3 \sigma_4} \times \mu_{\sigma_3 \sigma_4, \sigma_1} \mu_{\sigma_1, 0} = 2(N-1)\mu^2 \mu_{\sigma_2, 0}$, we find

$$\gamma^{(3)}(-3\omega; \omega, \omega, \omega) = -\frac{4\mu^2}{8\hbar^3(\omega^2 - \Omega^2)} \times \sum_{\sigma=1}^N \frac{|\mu_{0,\sigma}|^2}{3\omega - \Omega_\sigma + i\Gamma} \quad (6)$$

Note that eq. (6) does not exhibit size-enhancement, but predicts a simple scaling proportional to N , giving a THG intensity that scales like N^2 . (Size-enhancement does occur for $\omega \approx \Omega$ [19]. In the LFA we may, under the present detuning conditions, use $L_n(\omega) = 1$, so that only $L_n(3\omega)$ must be accounted for. Keeping only the resonant term in the molecular polarizability, we then immediately recover eq. (6) from eqs. (3)–(5). We conclude that for $\omega \approx \frac{1}{3}\Omega$, the THG signal predicted by the LFA is exact. This has recently also been noted for homogeneous systems with periodic boundary conditions [19,20]. The above derivation shows this equivalence to hold *irrespective of the disorder*. The underlying physical explanation is that the only resonance is the one of the signal beam with the one-exciton band, so that for a correct description of the resonance structure (or alternatively: of the intermolecular interactions) only the propagation of the signal, i.e. the linear susceptibility at 3ω , is needed. This is explicitly visible in eq. (6): the resonant factor (the summation over σ) is proportional to the linear polarizability. As the LFA in general exactly describes the linear susceptibility [18], it should thus also be exact for the present nonlinear technique. We believe that a similar rationale explains why recent second-harmonic generation experiments on Langmuir–Blodgett films

could be interpreted very accurately in terms of the LFA [21].

Fig. 1 displays the THG intensity as a function of laser frequency for aggregates of $N=40$ molecules, with $\Gamma=0.01|V|$ and disorder ranging from $D=0$ to $D=0.2|V|$. $\Omega_{k=1}$ denotes the frequency of the lowest one-exciton for a homogeneous chain, which has over 80% of the oscillator strength between the ground state and the one-exciton band [8]. For the lowest disorder values also two weaker one-exciton transitions are clearly resolved. With increasing disorder the main peak shows the usual disorder-induced red-shift [8] and broadens; as a result of motional narrowing [22], however, its fwhm stays much smaller than the molecular disorder D . We have analyzed the peak intensity as a function of disorder for different values of N ($N=20, 40, 60$). The results are displayed in fig. 2, where we give the normalized peak intensity, i.e. the peak intensity divided by N^2 , as a function of the exciton delocalization length at the position of the peak intensity. As a measure of the delocalization length we calculated $N_{\text{del}}=1.5/\mathcal{L}-1$, where $\mathcal{L} \equiv \langle \sum_n |\varphi_{en}|^4 \rangle_d$ is the inverse ratio of participation [8,23]. The top point of each data series corresponds to the homogeneous chain ($D=0$), where N_{del} equal N . Lower values of N_{del} correspond to increasing inhomogeneity, as disorder localizes the exciton states. It is clear from fig. 2 that for vanishing disorder the normalized peak intensity reaches a

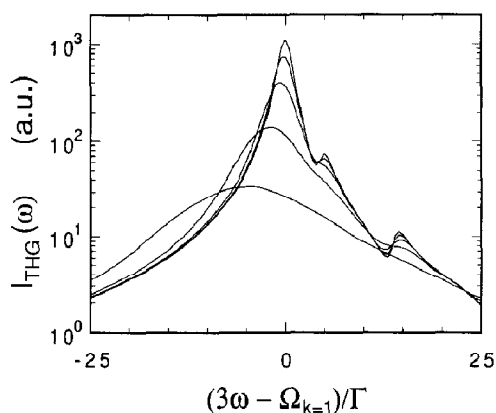


Fig. 1. Intensity of third-harmonic generation as a function of fundamental frequency ω for aggregates of 40 molecules with $\Gamma=0.01|V|$ and energetic disorder $D/|V|=0, 0.025, 0.05, 0.1$, and 0.2 from top to bottom. $\Omega_{k=1}$ is the frequency of the lowest one-exciton of the homogeneous chain.

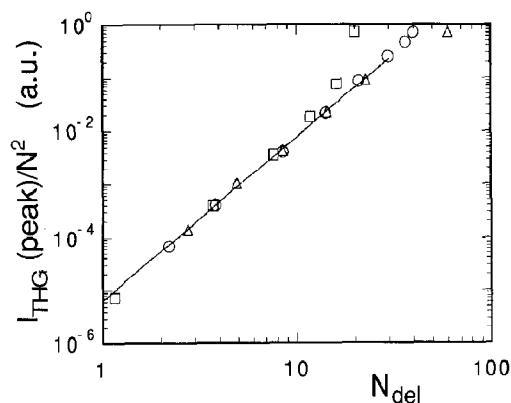


Fig. 2. Normalized peak intensity of THG versus exciton delocalization length for disordered aggregates of $N=20$ (\square), 40 (\circ), and 60 (\triangle) molecules with $\Gamma=0.01|V|$. From top to bottom the data points correspond to $D/|V|=0, 0.1, 0.2, 0.4, 1.0, 5.0$ ($N=20$), $D/|V|=0, 0.025, 0.05, 0.1, 0.2, 0.4, 1.0, 2.0$ ($N=40$), and $D/|V|=0, 0.1, 0.2, 0.4, 0.7, 1.5$ ($N=60$). The drawn line has a slope of 3.08 .

value that is independent of N , illustrating the fact that there is no size-enhancement. If N_{del} is appreciably less than N ($N_{\text{del}} \lesssim \frac{1}{2}N$), the delocalization length is no longer limited by the system size and determined by the disorder only. In that regime, we find that N_{del} scales approximately like $D^{-0.80}$ and, as is clear from fig. 2, all data then approach a simple power law for the peak intensity as a function of the delocalization length. The drawn line corresponds to

$$I_{\text{THG}}(\text{peak}) \propto N^2 N_{\text{del}}^{\beta}, \quad (7)$$

with $\beta=3.08$. Note that the proportionality to N^2 does not express size-enhancement, but results from the fact that the intensity is the square of the polarizability. A rationale for the scaling described by eq. (7) can be offered as follows. From eq. (6) it is seen that $\gamma^{(3)}(-3\omega; \omega, \omega, \omega)$ is dominated by the typical oscillator strength of a state at the exciton bandedge, multiplied by the density of states. It is known that the oscillator strength scales approximately like $D^{-0.7}$ [8], which, given the above scaling of N_{del} , is proportional to $N_{\text{del}}^{0.88}$. To estimate the scaling of the density of states, we think of the aggregate as N/N_{del} small intervals on which we may consider weakly scattered exciton states. From simple first-order perturbation theory in the disorder, it then follows that the oscillator strength carrying states on these inter-

vals (one per interval) are distributed over an energy range $D/\sqrt{N_{\text{del}}}$, where the last factor is an effect of motional narrowing [22]. Thus, the density of states scales like $N/D\sqrt{N_{\text{del}}} \propto NN_{\text{del}}^{0.75}$; this scaling is indeed found in the simulations. Combining the scaling of the oscillator strength and the density of states, we predict a value of β in eq. (7) of 3.26; the 6% deviation with the actual value is, in view of the crudeness of the arguments, not surprising.

3.2. Nonlinear absorption

The nonlinear absorption coefficient of an ensemble of aggregates is given by $A_{\text{NL}} \propto \text{Im} \langle \gamma^{(3)}(-\omega; \omega, \omega, -\omega) \rangle_d$. In contrast to the above discussed THG, it is easily shown that, on resonance, A_{NL} is not correctly described by local-field theory. This was recently demonstrated for homogeneous cyclic aggregates: line shape, magnitude, and size-scaling of the nonlinear absorption coefficient are found to differ profoundly from the exact theory [13]. Intuitively, one expects that for growing disorder the LFA improves, as interactions become less important due to the localization of the eigenstates. We have investigated this by simulating A_{NL} following from eqs. (2) and (3) for disorder values ranging from $D=0$ to $D=|V|$. Surprisingly, we find that on resonance the performance of the LFA does not at all improve over this disorder range. As an example, fig. 3 shows

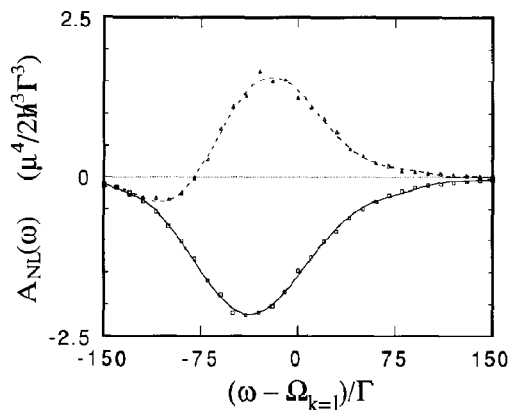


Fig. 3. Nonlinear absorption spectrum according to exact response theory (solid) and the local-field approximation (dashed) for aggregates of 40 molecules with $\Gamma=0.01|V|$ and $D=|V|$. Markers indicate the individual data obtained in the simulation.

the nonlinear absorption spectrum for $N=40$, $\Gamma=0.01|V|$, and $D=|V|$. Note that, whereas the exact theory predicts a net bleaching of the absorption line, the local-field approximation predicts extra absorption. A more detailed report on the nonlinear absorption lineshape, in which also other approximate theories are evaluated, will be published elsewhere [18].

We now turn to the size-scaling of the exact nonlinear absorption for disordered aggregates. Fig. 4 displays the peak value of the bleaching feature in the nonlinear absorption spectrum per molecule as a function of N_{del} . The data were obtained for aggregates of 10, 20, and 40 molecules. An important difference from fig. 2 is that for vanishing disorder (the top point of each data series) this quantity is not a constant, but scales like N , which demonstrates the on-resonance size-enhancement of the nonlinear absorption spectrum proportional to N^2 [3,4,17]. Fig. 4 clearly shows, however, that this enhancement breaks down if the disorder increases and N_{del} gets appreciably less than N . All data then approach one scaling line, which expresses the peak absorption as:

$$A_{\text{NL}}(\text{peak}) \propto NN_{\text{del}}^{\delta}, \quad (8)$$

with $\delta=2.36$. Note the proportionality to N , which marks the absence of enhancement. As the resonant nonlinear absorption coefficient is governed by the

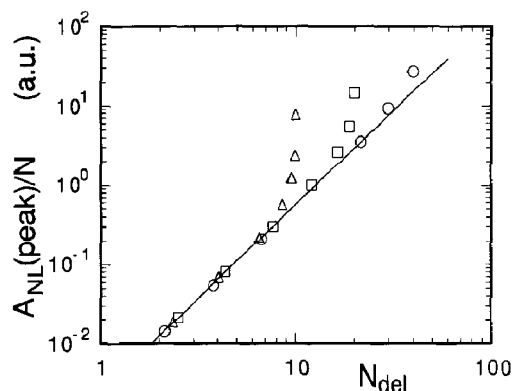


Fig. 4. Peak bleaching per molecule in the nonlinear absorption spectrum for aggregates of $N=10$ (Δ), 20 (\square), and 40 (\circ) molecules as a function of the exciton delocalization length. $\Gamma=0.01|V|$; the data points correspond from top to bottom to $D/|V|=0, 0.05, 0.1, 0.2, 0.4, 0.8, 1.6$ ($N=10$ and 20) and $D/|V|=0, 0.05, 0.1, 0.5, 1.0, 2.0$ ($N=40$). The drawn line has a slope of 2.36.

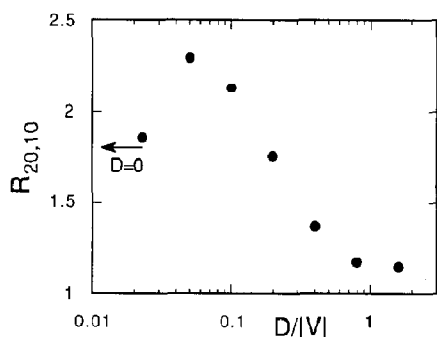


Fig. 5. Ratio of peak bleaching per molecule for the nonlinear absorption spectra of aggregates of 20 and 10 molecules as a function of disorder. $\Gamma=0.01|V|$.

square of the oscillator strength multiplied by the density of states, similar scaling arguments as the ones used in section 3.1 lead to a predicted value of 2.51 for δ . Finally, fig. 5 displays the ratio $R_{20,10}$ of the peak values of A_{NL} per molecule for aggregates of 20 and 10 molecules as a function of the disorder D . In the case of quadratic size-enhancement, $R_{20,10}$ should approximately equal 2 (the exact prediction is 1.86), which is indeed observed for $D=0$. The fact that in fig. 5, $R_{20,10}$ falls to unity for growing D , is a beautiful alternative demonstration of the breakdown of size-enhancement due to disorder. The initial increase of $R_{20,10}$ for weak disorder is not an artefact, but results from the fact that in that region motional narrowing is still stronger for larger aggregates, resulting in a larger peak density of states. Of course, this does not imply that a small amount of disorder is advantageous to obtain a large nonlinear response; in fact, it is clear from fig. 4 that weak disorder is already very effective in bringing down the peak response. The initial rise of $R_{20,10}$ only means that large aggregates suffer less from the effects of weak disorder than small ones.

4. Summary

In this Letter, we have presented numerical results for the third-harmonic generation and nonlinear absorption of disordered molecular aggregates. We have shown that, irrespective of disorder, the local-field approximation (LFA) is exact for techniques in which the only resonance is the one between the sig-

nal and the one-exciton band. By contrast, in the case of multiple resonances with the one- and (or) the two-exciton bands (as occurs for nonlinear absorption), the LFA does not correctly describe the optical response, not even for disorder ranging up to the intermolecular interaction, which is well above values relevant in typical experimental situations [8,9]. Finally, we have shown how disorder leads to the breakdown of size-enhancement of the hyperpolarizabilities and we have obtained and rationalized alternative scaling laws for the nonlinear response as a function of the extension of the exciton states.

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